

Polar Constituents of Coal Gasification Oil Samples

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In preliminary analyses by GC/MS, it was found that HYGAS oil samples contain a variety of compounds, including toluene, the start-up and make-up oil, aromatic hydrocarbons, phenols, anilines, pyridines, thiophenes, benzonitriles, and PNAs. Direct analysis of the mixture by GC/MS or capillary column GC/MS is at best difficult for at least two reasons: (1) Due to the large number (probably over 400) of compounds present in the mixture, many overlapping peaks occur, resulting in mass spectra that are often confusing; (2) Capillary columns that give good separation of non-polar compounds are not adequate for the separation of polar compounds. Therefore, there is a definite need for a preliminary separation into fractions of the complex mixtures in HYGAS oil samples.

For the separation of petroleum, fractional distillation, extraction, complex formation, and column chromatography, including adsorption, partition, and gel permeation, are among the methods that have been used. Each method has certain advantages and disadvantages: With fractional distillation, the toluene, which represents a major portion of a HYGAS oil sample, could be removed. However, this method suffers from the fact that any distillation, fractional or otherwise, requires heat and decomposition and reaction between components in the mixture typically takes place, altering the composition. With such extractions as the acid/base liquid-liquid type, recoveries of individual components of the mixture are not only variable but also often low, particularly with polar compounds; moreover, some matrix effects frequently occur affecting recoveries. Complex formation is not only too limited to be of use but also not applicable in this case since the complexes would not be chromatographable by GC. Column chromatography, although useful, suffers from being long and tedious and requires the use and workup of large amounts of solvent; it is not recommended for a large number of samples.

It can be stated, generally, that separations that can be done by column chromatography can also be done considerably better by HPLC. When compared to column chromatography, HPLC gives much better resolution, much shorter run times, and much less solvent. However, the amount of sample that can be processed per run is considerably less than with column chromatography. To overcome this disadvantage, several runs of the sample can be made with the attendant advantages of time, work-up of much less solvent, and resolution.

In the petroleum field, HPLC has been used predominantly for identification of components in a mixture or for fingerprinting oil samples. Little attention has been paid to the use of HPLC as a means of performing gross separations although, in certain instances, investigators have isolated peaks and identified the compound or compounds by GC/MS or mass spectrometry. Although HPLC/MS instruments are available, HPLC does not have the resolution capillary column GC has and, as a result, HPLC/MS is not as useful as capillary column GC/MS for the analysis of complex mixtures.

It was found that the use of the μ Bondapak NH₂ as a stationary phase in HPLC was excellent for the separation of non-polar or weakly polar compounds; however, with polar compounds, the phase was too retentive and, although moderately polar compounds might pass through the column with a gradient, highly polar compounds are retained. It is possible to backwash the highly polar compounds but separation into fractions of the polar compounds can not be achieved. However, if one is

interested only in non-polar or weakly polar PNAs, a nice separation according to the number of rings of the parent PNAs and their alkyl derivatives can be accomplished with μ Bondapak NH₂, as shown in Table 1.

Table 1. Retention Time Range of Selected Benzenoid PNAs and Alkyl PNAs as a Function of the Number of Rings (μ Bondapak NH₂, Hexane Solvent, Flow Programmed 1-4 mL/min)

Number of Rings	Retention Time Range (Minutes)	
	Noncondensed	Condensed
1	4.2 (1)	NA
2	5.0-5.8 (3)	NA
3	6.8-7.5 (7)	NA
4	9.3-10.9 (5)	7.7-8.3 (3)
5	13.7-15.1 (3)	11.5-12.1 (2)

() Number of compounds from which range was determined

NA Not Applicable

Such a separation into fractions can be very useful for identifying a complex mixture that contains predominantly compounds that are relatively non-polar, since GC conditions can be tailor-made to each fraction. It is particularly useful for identifying the higher PNAs.

Whereas HPLC with a μ Bondapak NH₂ column affords a good separation of non-polar compounds, it appeared that the weakly polar stationary phases, μ Bondapak Phenyl and μ Bondapak CN, might be more useful for separating the polar compounds into fractions. In experiments with these columns under a variety of conditions, it was found that, with μ Bondapak CN, a satisfactory separation could be accomplished using a rather complex gradient of hexane to THF, as shown in Figure 1.

Fraction 1 (Figure 1) contained a variety of the typical PNAs and alkyl PNAs, including naphthalenes, biphenyls, benzothiophenes, acenaphthenes, fluorenes, phenanthrenes, anthracenes, dibenzothiophenes, aceanthrenes, and pyrenes. (There was also a series of alkyl benzenes present in fraction 1.) Since the remaining fractions were more polar, they were derivatized with Tri-Sil Concentrate, BSA, or Methyl-8. Surprisingly, Fractions 2, 3, and 4 contained, along with some alkyl phenols, a number of hydroxy PNAs, including hydroxy styrenes, indans, benzofurans, indenes, naphthols, benzothiophenes, biphenyls, and fluorenes. In Table 2, a summary of the hydroxy PNAs and, in Figure 2, their retention time ranges on a 50 meter OV-101 column programmed from 20 to 240°C are shown. It can be seen from Table 2 that the more alkylation there is in the molecule the lower the fraction, as would be expected, since the compound would be less polar or more non-polar.

The mass spectra of the alkylated derivatives of the hydroxy PHAs typically had a M-15 ion as the base peak from loss of a methyl from the trimethyl silyl grouping. There was a M-31 peak indicative of a R-O-Si=CH₂ ion. The parent ion was also a prominent ion. Occasionally, a M-89 ion indicative of loss of (CH₃)₃SiO- was found. In the case of hydroxy biphenyls, an ion corresponding to the loss of the underderivatized phenyl ring is found.

Fractions 5 and 6 contained dihydroxy benzenes. No dihydroxy PNAs were found in these fractions, possibly, because they might not get through the column under the conditions used.

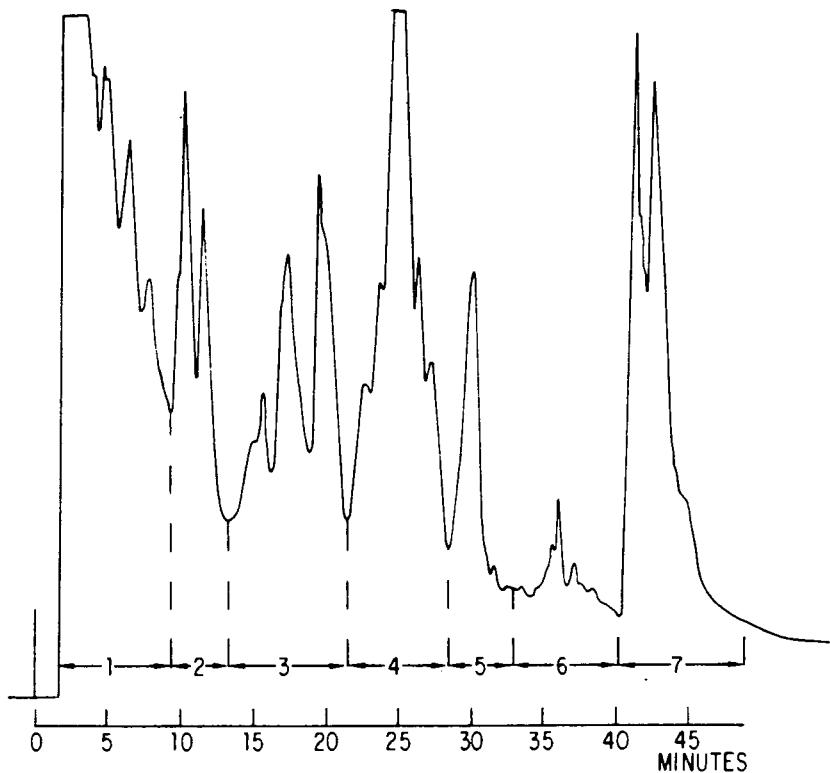


Figure 1. Hygas Oil Samples, HPLC on μ Bondapak CN Column, 2 mL/min Flow, 16 Minutes Hexane Alone, Linear Gradient, 0-1% in 10 Minutes, 1-5% in 10 Minutes, and 5-100% THF in Hexane in 10 Minutes; UV Detection at 254 nm

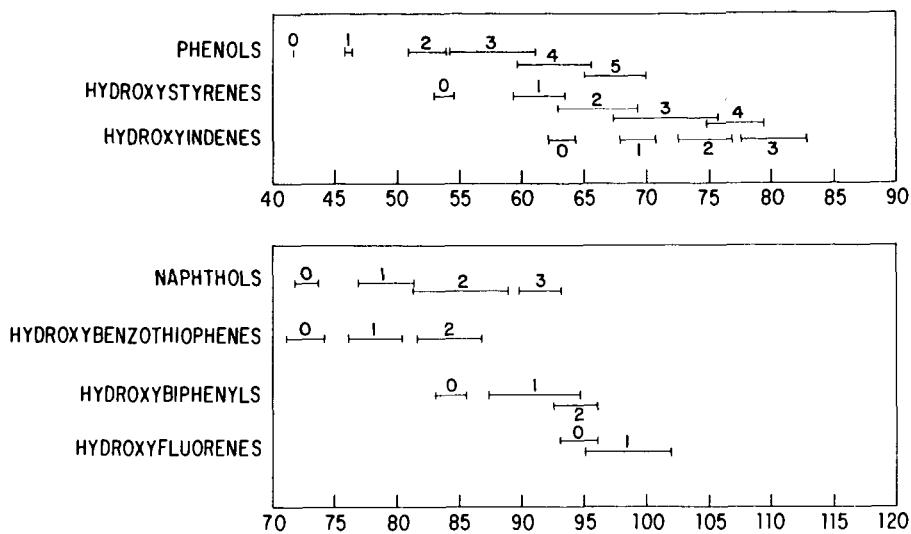


Figure 2. Retention Time Ranges of Some Phenols and Hydroxy PNAs, Derivatized with BSA, in Fractions 2,3, and 4

Table 2. Comparisons of Total Ion Count (in thousands) of Classes of Phenols and Hydroxy PNAs Versus Fraction

Type of Compound	Fraction			Type of Compound	Fraction		
	2	3	4		2	3	4
Phenols							
C ₀	-	-	2(1)	C ₀	-	47(2)	368(2)
C ₁	-	202(2)	4(2)	C ₁	-	277(6)	
C ₂	92(4)	669(5)	8(4)	C ₂	-	73(12)	95(10)
C ₃	213(9)	419(9)	-	C ₃	-	12(3)	2(1)
C ₄	84(8)	255(7)	-	Hydroxybenzothiophenes			
C ₅	9(3)	17(2)	-	C ₀	-	-	152(4)
Hydroxystyrenes							
C ₀	-	-	13(2)	C ₁	4(2)	15(3)	92(6)
C ₁	27(1)	97(3)	19(4)	C ₂	-	23(5)	42(10)
C ₂	144(8)	154(7)	19(7)	C ₃	-	-	3(1)
C ₃	80(15)	77(13)	3(1)	Hydroxybiphenyls			
C ₄	14(2)	8(4)	2(1)	C ₀	-	-	71(2)
Hydroxyindenes							
C ₀	-	19(2)	32(3)	C ₁	-	30(5)	101(7)
C ₁	-	24(8)	6(1)	C ₂	-	-	53(5)
C ₂	4(2)	8(4)	-	C ₃	2(1)	-	9(1)
C ₃	20(7)	2(1)	-	Hydroxyfluorenes			

() Number of compounds found, inside parentheses